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Science of the Total Environment 361 (2006) 267 – 278

Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Assessment of heavy metal accumulation in two species of *Tillandsia* in relation to atmospheric emission sources in Argentina

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Received 13 August 2004; received in revised form 24 October 2005; accepted 2 November 2005
Available online 20 December 2005

Abstract

The ability of *Tillandsia capillaris* Ruiz and Pav. f. *capillaris* and *Tillandsia permutata* A. Cast. to accumulate heavy metals was evaluated in relation to potential atmospheric emission sources in Argentina. The sampling areas ($n=38$) were chosen in the province of Córdoba, located in the center of Argentina, and categorized according to land use, anthropogenic activities and/or distance to potential heavy metal emission sources. In each sampling site, pools of 40–50 individuals of each species were made from plants collected along the four cardinal directions. The concentrations of V, Mn, Fe, Co, Ni, Cu, Zn, Pb and Br of these samples were measured by Total Reflection X-Ray Fluorescence (TXRF) analysis with Synchrotron Radiation. Each species was submitted to a cluster analysis in order to discriminate different groups of heavy metals as tracers of natural or anthropogenic sources. A Contamination Factor (CF) was calculated using the concentrations of the elements in each sample compared to their concentrations in the control samples. Finally, the rank coefficients of correlation between the CFs and the categorical variables characteristic of each site (land use and anthropogenic load) were analyzed. A positive correlation was found for *T. capillaris* between the CFs of V, Mn, Co, Ni, Cu and Zn and the urban-industrial category, whereas the CF values for Zn and Pb were positively correlated with the road category. In *T. permutata* there was a positive correlation between the CF of Zn and the urban-industrial category and the CF of Pb with the road category. We therefore conclude that *T. capillaris* is a more efficient metal accumulator in passive biomonitoring studies.

Keywords: Passive biomonitor; *Tillandsia capillaris*; *Tillandsia permutata*; Heavy metals accumulation; Argentina

1. Introduction

A significant deterioration of air quality has been observed for a long time in Argentina. However, it is only since the 1990s that environmental measurements and air-monitoring networks have begun, although only in a few cities. Today, due to financial difficulties, no measurements of air pollution are carried out in Córdoba city even though there are visible problems of contamination due to traffic congestion and the concentration of industrial activities. Furthermore, for some years, air pollution has also been found in remote areas of Argentina as a consequence of agricultural practices, mining and long-range transport (Moretton et al., 1996). Thus, the use of pollution biomonitors is an important contribution to Argentina where

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doi:10.1016/j.scitotenv.2005.11.005

measurements of particulate matter or other atmospheric pollutants in large areas require expensive technical equipment currently unavailable (Pignata et al., 2002). Biomonitors have several advantages concerning the detection of polluting emission sources such as low costs, the possibility to register the effects of pollution for longer periods of time, and the possibility of monitoring many sites simultaneously.

In Argentina, studies on the multielemental composition of the environment using bioindicators have mainly been undertaken using lichens (Calvelo et al., 1997, 1998, 2002; Carreras and Pignata, 2001, 2002; Jasan et al., 2004; Pignata et al., 2004; Carreras et al., 2005), and one species of the *Tillandsia* genus (Pignata et al., 2002). Epiphytic plants are efficient air pollution biomonitors because they obtain their nutrients from the atmosphere and have no contact with the earth. Therefore, the elemental composition of their tissues and their physiological responses largely reflect the atmospheric input of air pollutants such as toxic gases and heavy metals (Figueiredo et al., 2001).

Regarding the bioindicating capacity of atmospheric pollution by epiphytic vascular plants of the *Tillandsia* genus, *Tillandsia usneoides* has proved to be an efficient atmospheric accumulator of Hg in the areas surrounding a chlor-alkali plant in Rio de Janeiro (Brazil) (Calasans and Malm, 1997). This species has been previously used for the evaluation of the content of fluoride in rain water (Strehl and Arndt, 1989) and the presence of Hg in urban areas (Malm et al., 1998). Also, *T. aeranthos* and *T. recurvata* have been employed in Porto Alegre (Brazil) to assess atmospheric levels of sulfur and heavy metals in industrialized and residential areas (Flores, 1987). In Colombia, the airborne heavy metal

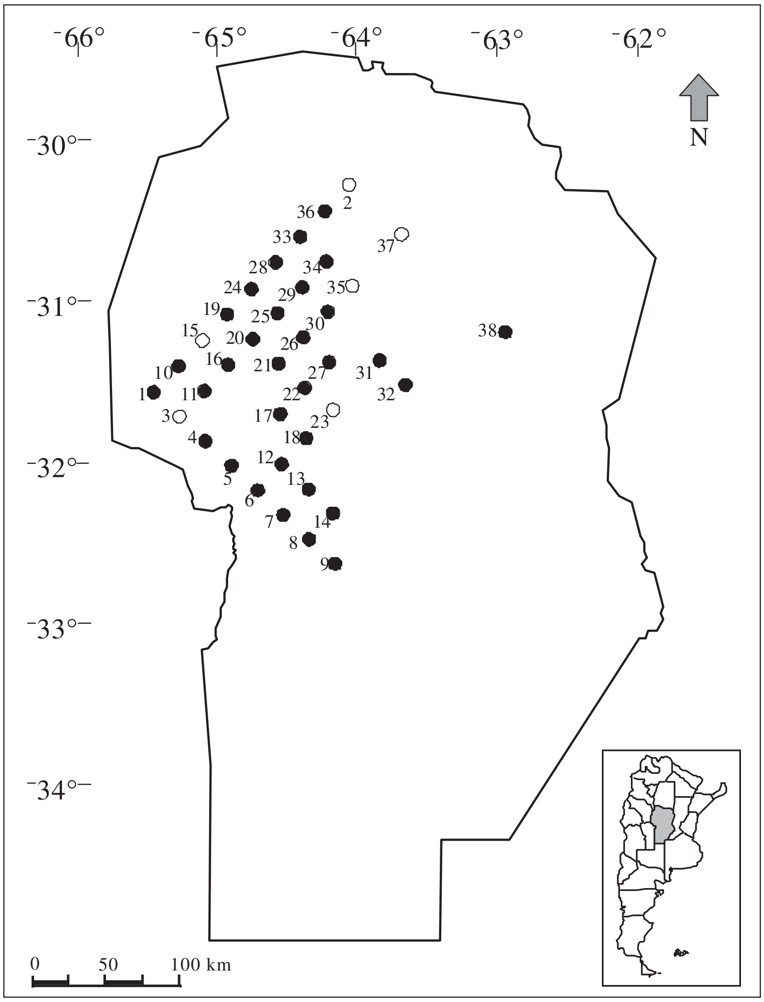

Fig. 1. Localization of the study area and the individual sampling sites in the province of Córdoba, Argentina. (● Sites for *T. capillaris* and *T. permutata*; ○ sites for *T. capillaris* only).

deposition in the highly industrialized Cauca Valley was examined using *T. recurvata* as an accumulative indicator (Schrimpff, 1984).

In Argentina there are many species of *Tillandsia*, among which *T. capillaris* has been studied as a biomonitor of the atmospheric quality of the province of Córdoba (Pignata et al., 2002). For this study we choose to compare the response of *T. capillaris* with that of *T. permutata* because preliminary studies indicated that these two species differed in their metal accumulation capacity.

Hence, the aim of this study was to compare the bioindicating capacity of *T. capillaris* and *T. permutata* regarding their capacity to accumulate heavy metals and Br and to determine whether a relation exists between the concentrations of these elements and the presence of atmospheric emission sources in the study area.

2. Materials and methods

2.1. Study area

The sampling points were located in the province of Córdoba, in the centre of Argentina (Fig. 1). The morphology of the land in this area is highly variable, ranging from a mean elevation of around 100 m above sea level (m.a.s.l.) in the southeast to over 2500 m.a.s.l. in the midwest (Fig. 2). The most important cities closest to the sampling sites are: Córdoba (1,267,521 inhabitants), Río Cuarto (144,021 inhabitants), Villa María (72,162 inhabitants), San Francisco (58,779 inhabitants), Villa Carlos Paz (56,407 inhabitants), Río Tercero (44,715 inhabitants), Alta Gracia (42,538 inhabitants), Jesús María (37,185 inhabitants), Villa Dolores (28,009 inhabitants) and Cruz de Eje (28,166 inhabitants). The main industrial activity of the city of

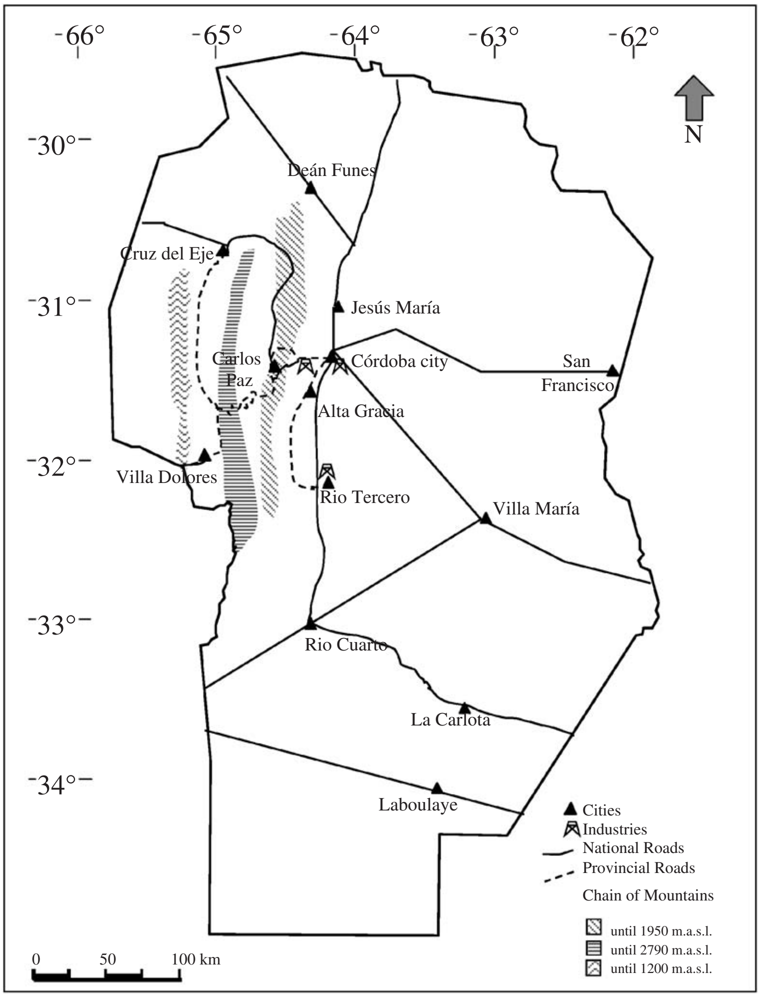

Fig. 2. Locations of the most important cities, roads, industries and mountain ranges in the study area in the province of Córdoba, Argentina.

Córdoba is metallurgic, although there is also a cement factory 15 km to the west of the city with an incinerator of dangerous industrial wastes. The city of Río Tercero is located in the south of the sampling area, and has important petrochemical and chemical industries (Fig. 2). However, there are no data on their atmospheric emissions.

2.2. Biological material and sampling procedures

Two species of epiphytic plants were selected as biomonitors: *Tillandsia capillaris* Ruiz and Pav. f. *capillaris* and *Tillandsia permutata* A. Cast. Adult plants of *T. capillaris* and *T. permutata* of approximately the same diameter were collected at 38 sampling points, from December 4th, 2000 to February 28th, 2001 (Fig. 1). The samples were taken using plastic gloves to avoid any sort of contamination and immediately placed into paper bags (Sloof, 1993). Sampling was only done if there had been no rain during the previous five days. Pools composed of 40–50 individuals of each species were randomly collected in each sampling site along the four cardinal directions, in a quadrant of 100 × 100 m. Back in the laboratory, pools of each site were divided into three sub-samples (of approximately 15–20 plants each). Any foreign materials and particles were eliminated both manually and with compressed air. The leaves of the plants of each sub-sample were separated, mixed together and kept in the dark at −15 °C until analysis. The heavy metal content in each sub-sample was individually analyzed (Section 2.4).

2.3. Characterization of the sampling sites

The details of the land use, anthropogenic activities and/or proximity to heavy metal emission sources were characterized for each sampling site chosen in the province of Córdoba (Fig. 2). Each site was graded on a scale of 1–3, where 1 represents the condition with the lowest anthropogenic activity and/or polluting emission sources and 3 the condition with the highest contaminating anthropogenic activities. The variables taken into consideration to score the areas were:

(a) Agricultural: this variable was taken into consideration due to the fact that Argentina has vast areas dedicated to extensive agriculture in which phosphate fertilizers are used. The categories were: (1) no agricultural activity, (2) low agricultural activity, (3) areas in which the main activity was agriculture.

(b) Urban-Industrial: in this variable the presence and/or closeness to cities with contaminants emanated from chemical, petrochemical and metallurgic–metallic industries was considered. Category (1) includes the sites located in areas with no industries or urban centers. Category (2) includes the sampling sites close to urban centers (less than 10 km) with a population of 5000–40,000 people with some small industries. Category (3) includes the areas close to large industries and cities with a population of over 40,000.

(c) Roads: in Córdoba city, traffic is considered the main source of urban air pollution. In fact, about

Table 1
Characterization of the environmental variables of each sampling point according to pollutant emission sources and elevation (m.a.s.l.)

Site	Elevation	Agricultural	Urban-Industrial	Roads
1 (Control)	440	1	1	1
2	525	3	1	1
3	369	2	1	1
4	636	2	1	1
5	656	2	1	2
6	962	2	1	1
7	733	2	1	1
8	732	2	1	1
9	556	3	1	3
10	1011	2	1	1
11	1049	2	1	2
12	813	2	2	2
13	835	2	3	2
14	582	3	1	3
15	848	2	1	2
16	1628	1	1	1
17	960	2	1	1
18	716	3	1	1
19	1080	1	1	1
20	1037	2	1	1
21	630	1	2	2
22	608	2	3	2
23	395	3	1	1
24	1017	1	1	1
25	524	1	2	3
26	860	1	2	2
27	405	1	3	3
28	1143	2	1	1
29	730	2	1	1
30	605	3	2	3
31	250	2	1	1
32	195	3	1	1
33	618	3	1	3
34	605	3	1	3
35	477	3	1	1
36	429	3	2	3
37	104	3	1	1
38	140	3	1	1

80% of urban air pollution arises from mobile sources rather than industrial smokestacks (Olcese and Toselli, 2004). Due to the presence of roads with heavy traffic in the study area, we considered it important to establish a category in which the contribution of metals from vehicular traffic to the atmospheric contamination could be assessed. This variable was categorized in each site according to the distance from the center of each sampling area to roads with high, medium and low levels of traffic (Table 1). Therefore, category (1) represented the absence of nearby roads (more than 3 km away), category (2) included sites near secondary roads (within 3 km) with scarce vehicular traffic and category (3) included the sites near (within 3 km) to main roads (national main roads with circulation of long distance buses, heavy trucks, cargo vehicles, etc.).

(d) Elevation: this variable was considered in order to evaluate whether some of the elements analyzed have a pattern of distribution dependent on elevation. As each area is composed of different levels this variable was recorded in meters above sea level.

Table 2
Mean values±standard deviation of the concentration of V, Mn, Fe, Co and Ni (μg g super $^{-1}$ FW) measured in *T. capillaris* leaves (n=3)

Site	V	Mn	Fe	Co	Ni
	Mean±S.D.	Mean±S.D.	Mean±S.D.	Mean±S.D.	Mean±S.D.
1 (Control)	0.34±0.07	20.60±0.23	174.98±58.74	0.08±0.02	0.08±0.02
2	1.18±0.17	33.96±4.33	295.24±2.30	0.14±0.01	0.29±0.27
3	1.19±0.06	24.55±0.83	331.29±33.94	0.13±0.03	0.16±0.04
4	0.65±0.15	15.06±1.65	153.70±12.86	0.07±0.03	0.12±0.10
5	0.51±0.14	21.77±2.89	196.74±46.42	0.10±0.01	0.12±0.04
6	1.28±0.26	20.05±3.07	191.21±24.91	0.08±0.01	0.19±0.03
7	0.54±0.10	11.75±0.24	127.54±40.79	0.06±0.02	0.09±0.07
8	0.64±0.14	15.72±0.38	126.68±27.46	0.06±0.02	0.16±0.03
9	0.90±0.21	14.68±0.57	179.96±30.99	0.08±0.02	0.09±0.01
10	0.51±0.05	14.49±2.04	140.93±34.92	0.07±0.01	0.38±0.11
11	0.92±0.15	21.89±0.59	408.11±24.76	0.19±0.01	0.24±0.09
12	0.36±0.06	11.36±0.03	129.60±29.75	0.06±0.01	0.15±0.06
13	1.37±0.01	21.09±1.47	193.28±30.89	0.09±0.02	0.21±0.13
14	0.70±0.12	16.18±0.91	198.35±36.19	0.08±0.02	0.14±0.01
15	0.49±0.09	10.52±0.28	123.80±4.49	0.06±0.01	0.14±0.01
16	1.20±0.31	49.07±3.55	308.29±6.62	0.14±0.01	0.27±0.01
17	1.20±0.05	17.94±2.85	216.34±63.45	0.09±0.02	0.10±0.01
18	0.76±0.14	15.14±4.02	213.49±62.03	0.10±0.03	0.10±0.08
19	1.09±0.33	19.99±5.95	348.66±93.80	0.15±0.04	0.30±0.11
20	0.71±0.18	13.67±1.04	125.85±35.01	0.06±0.02	0.10±0.01
21	1.29±0.48	28.03±4.15	372.66±65.34	0.16±0.04	0.53±0.15
22	0.86±0.05	24.66±1.18	182.13±9.58	0.10±0.01	0.46±0.07
23	0.63±0.16	15.56±0.93	159.76±20.68	0.08±0.01	0.06±0.01
24	2.14±0.34	34.21±2.45	442.20±22.16	0.20±0.04	0.21±0.06
25	1.76±0.49	27.84±7.01	276.04±64.75	0.14±0.04	0.16±0.09
26	0.57±0.13	9.55±0.44	99.04±10.75	0.05±0.01	0.12±0.06
27	0.71±0.04	8.81±2.20	122.36±11.61	0.06±0.03	0.11±0.06
28	1.17±0.43	26.11±4.20	245.30±20.59	0.11±0.01	0.47±0.07
29	3.16±0.51	35.55±0.23	569.60±142.19	0.26±0.06	0.16±0.05
30	1.84±0.28	31.88±3.14	196.35±47.77	0.09±0.02	0.11±0.01
31	0.67±0.08	22.50±1.51	111.44±6.86	0.06±0.01	0.06±0.01
32	0.96±0.31	19.05±0.62	235.78±21.04	0.11±0.01	0.15±0.03
33	0.70±0.27	23.99±6.47	231.92±66.49	0.11±0.02	0.13±0.03
34	0.65±0.13	40.17±3.21	284.93±35.16	0.14±0.04	0.33±0.13
35	1.04±0.13	42.82±7.59	289.83±38.67	0.15±0.01	0.43±0.11
36	0.46±0.06	18.53±2.17	138.11±47.72	0.07±0.03	0.33±0.06
37	1.38±0.10	51.12±15.39	220.31±84.63	0.11±0.04	0.23±0.04
38	0.46±0.09	9.57±0.55	97.58±0.86	0.04±0.01	0.09±0.03
Mean (n=38)	0.97	22.62	222.62	0.10	0.20

Sampling site 1, located in the Natural Reserve of Chancaní (Fig. 1), was considered the control site as it is a protected area with no human activities. Apart from being a Natural Reserve, this area is separated from the main urban and industrial areas by three mountain ranges (Fig. 2): the Sierras Chicas (1950 m), the Sierras Grandes (2790 m) and the Sierras de Pocho (1200 m) that isolate the area from the atmospheric contamination of urban centres, maintaining it in pristine conditions. This area is also protected by the legislation of the government of the province of Córdoba since 1983.

2.4. Elemental analysis by TXRF

Leaves of the *Tillandsia* plants from each sub-sample were dried to constant weight in an oven at 50±2 °C, and a 2 g dry weight sample of this material was taken for the multielemental analysis by Total Reflection X-Ray Fluorescence (TXRF) using Synchrotron Radiation. The dry material was ground and reduced to ashes at 500 °C for 4 h. The ashes were digested with HCl (18%):HNO_3 (3:1) at 25±2 °C and the solid residues were then separated by centrifugation. Finally, the volume was adjusted to 25 ml with Milli-Q water and 10 ppm of a Ge solution was added as an internal standard. Aliquots of 5 μl were taken from this solution and dried on an acrylic support. For quality control, samples of "Hay IAEA-V-10" standard reference material were prepared in the same way as described for the samples. Standard solutions with known concentrations of different elements and with Ge as an internal standard were prepared for the calibration of the system.

The samples were measured for 200 s, using the total reflection setup mounted at the X-ray fluorescence beamline of the National Synchrotron Light Laboratory (LNLS), Campinas, SP, Brazil. A polychromatic beam of approximately 0.3 mm wide and 2 mm high was used for excitation. In the X-ray detection a Si(Li) detector was used with an energy resolution of 165 eV at 5.9 keV.

2.5. Contamination factor

Contamination factors (CFs) were calculated for each element using the arithmetic mean of its concentration in each biomonitor, for each sampling point. More specifically, the factor was calculated dividing the concentration of each element in the biomonitor by the concentration of the element in the control site (Conti and Cechetti, 2001). In order to minimize the effect of soil deposition, and considering the fact that Fe is the main element present in the soil of the study area, the concentration of each element was normalized with respect to Fe according to the following formula:

$$CF_j = (x/\mathrm{Fe})_{\mathrm{site}\ j}/(x/\mathrm{Fe})_{\mathrm{site\ control}}$$

where CF_j is the contamination factor in site j, $(x/\mathrm{Fe})_{\mathrm{site}\ j}$ is the ratio between element x and Fe in site j; $(x/\mathrm{Fe})_{\mathrm{site\ control}}$ is the ratio between element x and Fe in the control site. Thus, the values of CF indicate the enrichment of a certain element with respect to the soil of the sampling site as well as its increase compared to the control site.

Table 3
Mean values±standard deviation of the concentration of Cu, Zn, Pb and Br (μg g^{-1} FW) measured in *T. capillaris* leaves (n=3)

Site	Cu	Zn	Pb	Br
	Mean±S.D.	Mean±S.D.	Mean±S.D.	Mean±S.D.
1 (Control)	0.46±0.10	2.03±0.27	0.26±0.04	0.75±0.33
2	0.76±0.31	3.30±0.09	0.97±0.10	3.30±0.14
3	0.85±0.17	2.79±0.16	0.20±0.06	3.71±1.25
4	0.74±0.08	5.26±1.60	0.30±0.03	2.27±0.57
5	1.95±0.07	4.05±0.45	0.58±0.02	2.87±0.95
6	0.70±0.02	2.77±0.19	0.32±0.00	2.23±0.41
7	0.39±0.14	1.85±0.22	0.53±0.43	1.15±0.25
8	0.51±0.25	1.93±0.35	0.28±0.08	2.67±0.79
9	0.44±0.12	2.02±0.22	0.32±0.01	0.66±0.17
10	0.84±0.42	2.58±0.34	0.40±0.03	1.99±0.16
11	0.85±0.06	6.91±0.98	0.78±0.07	3.74±0.15
12	1.30±0.47	3.23±0.07	0.33±0.02	1.19±0.24
13	0.30±0.03	2.02±0.11	0.30±0.01	0.97±0.18
14	0.51±0.10	3.40±0.29	0.89±0.05	2.00±0.47
15	0.79±0.25	4.10±0.97	0.84±0.03	2.73±0.74
16	2.05±0.19	4.94±0.26	0.63±0.16	4.64±0.41
17	0.37±0.08	2.29±0.34	0.37±0.06	2.38±0.62
18	0.39±0.08	2.08±0.61	0.31±0.14	4.46±0.52
19	1.11±0.56	7.10±1.85	0.60±0.01	2.23±0.67
20	2.31±0.90	4.22±1.52	0.37±0.02	1.08±0.31
21	1.10±0.18	9.57±1.38	1.07±0.11	4.08±0.40
22	0.69±0.12	4.46±0.95	0.58±0.01	2.71±0.53
23	0.38±0.01	2.03±0.38	0.33±0.02	1.02±0.16
24	0.89±0.01	6.30±1.65	1.17±0.25	2.96±0.66
25	1.50±0.47	4.66±1.23	0.59±0.18	1.51±0.16
26	0.56±0.30	2.89±0.82	0.25±0.07	0.86±0.13
27	0.59±0.01	5.79±0.41	0.18±0.06	4.34±1.02
28	0.62±0.03	3.72±0.29	0.46±0.02	2.92±0.64
29	1.53±0.33	7.71±1.05	0.59±0.14	3.52±0.44
30	1.06±0.35	2.73±0.75	0.35±0.04	3.29±0.23
31	0.25±0.05	2.12±0.07	0.20±0.05	1.88±0.65
32	0.49±0.05	3.77±1.01	0.33±0.04	3.50±0.83
33	1.40±0.19	6.00±1.21	0.79±0.20	3.23±0.64
34	1.03±0.31	6.35±0.64	0.91±0.27	3.54±0.13
35	0.90±0.27	3.84±0.49	0.78±0.18	2.83±0.65
36	0.50±0.10	5.45±1.29	1.16±0.45	1.97±0.49
37	2.41±0.77	4.21±0.67	0.38±0.11	2.52±0.82
38	0.29±0.04	1.66±0.25	0.19±0.04	1.13±0.07
Mean (n=38)	0.89	4.00	0.52	2.49

Table 4
Mean values ± standard deviation of the concentration of V, Mn, Fe, Co and Ni (μg g^{-1} FW) measured in *T. permutata* leaves (n=3)

Site	V	Mn	Fe	Co	Ni
	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.
1 (Control)	0.82 ± 0.26	24.53 ± 0.86	440.87 ± 168.73	0.17 ± 0.08	0.18 ± 0.08
4	0.98 ± 0.18	14.24 ± 0.87	200.25 ± 73.55	0.11 ± 0.04	0.23 ± 0.16
5	0.64 ± 0.31	12.01 ± 0.17	121.77 ± 52.59	0.08 ± 0.01	0.09 ± 0.01
6	1.23 ± 0.35	12.91 ± 0.11	244.33 ± 32.69	0.11 ± 0.01	0.17 ± 0.04
7	0.76 ± 0.08	16.61 ± 0.57	127.61 ± 1.64	0.07 ± 0.01	0.14 ± 0.02
8	1.09 ± 0.27	19.06 ± 0.39	358.22 ± 64.54	0.16 ± 0.02	0.35 ± 0.13
9	0.82 ± 0.32	16.07 ± 3.38	178.06 ± 8.18	0.08 ± 0.01	0.14 ± 0.06
10	0.34 ± 0.18	14.83 ± 0.71	138.13 ± 16.71	0.07 ± 0.03	0.14 ± 0.03
11	0.53 ± 0.27	21.26 ± 0.55	222.13 ± 25.85	0.10 ± 0.01	0.19 ± 0.07
12	1.43 ± 0.62	24.02 ± 1.73	246.42 ± 13.11	0.11 ± 0.02	0.42 ± 0.15
13	2.00 ± 0.02	41.72 ± 0.71	255.30 ± 36.50	0.13 ± 0.01	1.13 ± 0.51
14	1.70 ± 0.55	18.51 ± 0.40	229.47 ± 53.19	0.10 ± 0.02	0.10 ± 0.03
16	1.02 ± 0.17	40.44 ± 0.02	272.16 ± 52.99	0.14 ± 0.02	0.46 ± 0.03
17	1.73 ± 0.58	24.41 ± 0.06	462.24 ± 203.41	0.19 ± 0.07	0.10 ± 0.01
18	0.42 ± 0.05	13.24 ± 0.13	188.27 ± 51.17	0.08 ± 0.01	0.08 ± 0.01
19	0.84 ± 0.56	26.61 ± 0.01	267.01 ± 42.88	0.12 ± 0.04	0.14 ± 0.11
20	1.36 ± 0.22	14.49 ± 1.49	238.96 ± 74.74	0.09 ± 0.01	0.17 ± 0.02
21	1.35 ± 0.07	34.11 ± 0.60	384.31 ± 29.11	0.17 ± 0.01	0.26 ± 0.13
22	1.27 ± 0.42	28.88 ± 0.70	369.40 ± 48.49	0.17 ± 0.02	0.13 ± 0.04
24	1.81 ± 0.19	30.21 ± 8.14	390.66 ± 23.98	0.18 ± 0.01	0.22 ± 0.09
25	1.75 ± 0.04	22.21 ± 2.28	502.22 ± 43.48	0.23 ± 0.02	0.37 ± 0.04
26	1.63 ± 0.57	15.98 ± 0.06	146.05 ± 7.02	0.07 ± 0.01	0.16 ± 0.09
27	0.62 ± 0.20	15.34 ± 1.34	146.84 ± 18.30	0.07 ± 0.01	0.07 ± 0.01
28	1.43 ± 0.14	35.79 ± 4.46	321.85 ± 20.31	0.16 ± 0.01	0.13 ± 0.07
29	2.00 ± 0.39	22.43 ± 1.18	331.80 ± 75.26	0.16 ± 0.02	0.27 ± 0.08
30	1.09 ± 0.00	33.65 ± 3.25	248.73 ± 85.73	0.13 ± 0.05	0.13 ± 0.02
31	0.85 ± 0.29	17.17 ± 1.19	163.64 ± 30.65	0.08 ± 0.01	0.04 ± 0.01
32	0.69 ± 0.23	17.49 ± 2.83	185.39 ± 82.39	0.09 ± 0.04	0.08 ± 0.01
33	1.34 ± 0.33	20.88 ± 0.21	183.60 ± 6.55	0.07 ± 0.02	0.17 ± 0.12
34	1.45 ± 0.27	38.76 ± 0.61	429.36 ± 39.38	0.19 ± 0.03	0.93 ± 0.52
36	0.50 ± 0.26	16.84 ± 1.21	131.93 ± 21.06	0.05 ± 0.01	0.17 ± 0.01
38	0.42 ± 0.02	9.62 ± 1.60	91.60 ± 22.79	0.04 ± 0.02	0.09 ± 0.06
Mean (n=32)	1.12	22.32	256.83	0.12	0.23

2.6. Data analysis

The elemental data from each sample of *Tillandsia* collected in each site were analyzed with a cluster analysis. Categorical environmental data were standardized to a mean of zero and a unit variance, ranked, and Spearman's rank coefficient of correlation was calculated in order to study the relationship between the concentration of the element and the environmental variables. Pearson's coefficient of correlation was calculated for the variable elevation.

3. Results

Tables 2 and 3 show the results of the elements measured in *T. capillaris* (38 sites) and Tables 4 and 5 show the results for *T. permutata* (32 sites). The concentrations of the elements were similar in both species. The main elements found were Fe and Mn which are the main elements found in Argentine soils (Gaiero et al., 2003). The average concentration of Br was similar to the values reported by Figueiredo et al. (2001) for samples of *T. usneoides* transplanted in Sao Paulo (Brazil) but the concentrations of V, Mn, Fe, Co and Zn were lower than the values described by these authors. On the other hand, although the concentrations of Fe in our study were higher than the values found by Benzing and Bermudes (1991) in samples of *T. balbisiana*, *T. paucifolia* and *T. utriculata* collected in south Florida, the levels of Cu, Mn and Zn were similar to the concentrations reported by these authors. The mean values determined in this study for Cu, Pb, Zn and Co were also similar to those found by Pignata et al. (2002) in *T. capillaris*, whereas the concentrations of Ni, Mn and Fe were lower. The concentrations of Fe and Mn in *T. capillaris* and *T. permutata* were similar to those

Table 5
Mean values±standard deviation of the concentration Cu, Zn, Pb and Br (μg g^{-1} FW) measured in *T. permutata* leaves (*n*=3)

Site	Cu	Zn	Pb	Br
	Mean±S.D.	Mean±S.D.	Mean±S.D.	Mean±S.D.
1 (Control)	1.06±0.40	2.70±0.91	0.16±0.02	2.17±0.12
4	0.82±0.23	2.47±0.77	0.44±0.22	3.09±0.97
5	0.51±0.02	1.80±0.03	0.36±0.03	2.71±0.67
6	1.01±0.17	4.22±1.61	0.35±0.08	2.83±0.89
7	0.80±0.36	2.45±0.14	0.41±0.06	0.91±0.08
8	1.67±0.70	2.88±1.10	0.25±0.19	1.90±0.03
9	0.42±0.13	2.75±0.31	0.34±0.04	1.57±0.11
10	0.92±0.33	2.50±0.18	0.47±0.02	4.21±0.15
11	1.05±0.22	2.91±0.10	0.81±0.01	3.01±0.63
12	1.11±0.20	4.22±0.49	0.39±0.20	3.49±0.19
13	1.36±0.18	6.15±1.77	0.89±0.18	3.03±0.10
14	1.31±0.64	4.10±0.91	1.02±0.10	3.08±0.29
16	1.11±0.06	4.49±0.47	0.60±0.05	3.15±0.46
17	1.15±0.35	3.93±0.21	0.40±0.05	3.75±0.94
18	0.48±0.31	2.34±1.02	0.28±0.04	1.95±0.63
19	0.63±0.04	3.76±0.73	0.48±0.18	1.84±0.33
20	0.77±0.11	3.61±0.54	0.35±0.07	4.07±1.62
21	1.49±0.64	8.04±1.52	0.79±0.08	3.03±0.14
22	2.10±0.56	5.87±0.30	0.87±0.02	4.40±2.34
24	1.55±0.25	4.41±0.93	0.71±0.15	2.19±0.30
25	0.63±0.06	3.14±0.41	0.88±0.17	3.86±0.03
26	0.96±0.52	3.01±0.72	0.37±0.03	2.31±0.24
27	1.33±0.62	4.22±1.40	0.55±0.07	2.61±0.57
28	1.20±0.12	5.28±0.62	1.19±0.17	2.52±0.09
29	1.78±0.58	5.23±0.87	0.81±0.04	3.22±0.73
30	0.51±0.05	2.68±0.22	0.49±0.02	2.26±1.47
31	0.29±0.01	1.62±0.01	0.25±0.01	4.09±0.01
32	1.39±0.35	3.86±1.72	0.30±0.01	1.53±0.64
33	0.38±0.03	4.56±0.10	0.62±0.14	3.40±0.52
34	0.84±0.30	5.80±1.02	0.70±0.29	5.36±0.02
36	0.47±0.19	4.82±1.10	0.37±0.01	1.96±0.08
38	1.08±0.38	1.98±1.06	0.18±0.03	0.96±0.22
Mean (*n*=32)	1.01	3.81	0.53	2.83

found by Husk et al. (2003) in *T. usneoides* in Central Florida, although these authors found significant differences in the concentrations of metals between plants growing on different host trees.

It is important to note that in our study the concentrations of Fe, Mn, Cu and Zn, cationic oligoelements necessary for the normal development of the plants, were not higher than the normal natural concentrations previously cited for *Tillandsia* (Salisbury and Ross, 1992).

3.1. Hierarchical cluster analysis

In order to discriminate the groups of heavy metals as tracers of natural or anthropogenic sources, an explorative hierarchical cluster analysis was performed with the data set of the elements according to Manta et al. (2002). In the case of *T. capillaris* the results (Fig. 3) allowed the elements to be divided into two groups: V, Fe and Co (closely associated among themselves), Mn, Br and Cu constitute Group I, and Ni, Zn and Pb, Group II. These results suggest that the elements in Group I have a natural origin, while Group II includes metals with an anthropogenic origin. Pignata et al. (2002) studied the accumulation of Fe, Mn and Co in the same species and in the same area, and attributed the accumulation of these elements to their presence in the soil, in accordance with the studies of Gaiero et al. (2003) for atmospheric particulate matter collected in Argentina. These authors reported that together with Al, the source of Fe and Mn in eolic dust samples is mainly from natural weathered materials.

The cluster analysis undertaken for *T. permutata* (Fig. 4) also distinguished two groups. However, in this species Br and Mn are associated with the group of elements that have a clear anthropogenic origin (Group

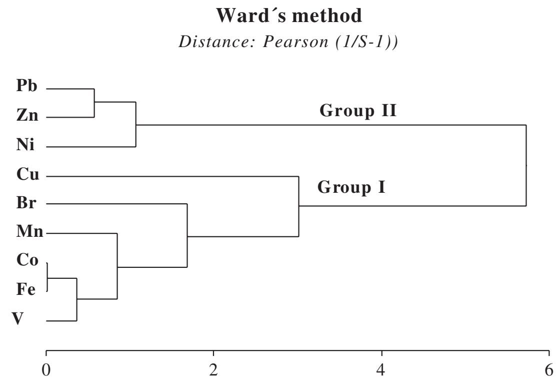

Fig. 3. Results of the hierarchical cluster analysis (dendrogram) of the heavy metal concentrations in *T. capillaris,* including the control site (*n*=38).

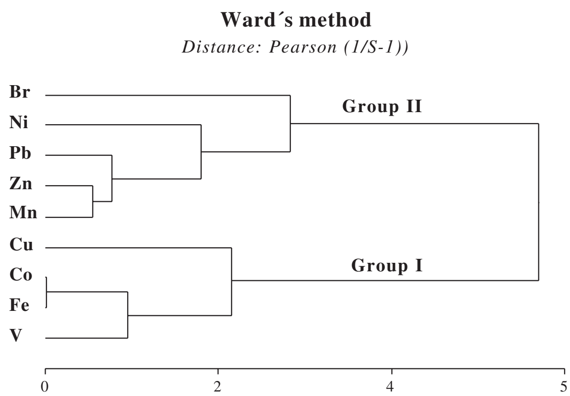

Fig. 4. Results of the hierarchical cluster analysis (dendrogram) of the heavy metal concentrations in *T. permutata*, including the control site (*n*=32).

Table 6
Contamination Factor (CFs) values of V, Mn, Co, Ni, Cu, Zn, Pb and Br measured in *T. capillaris* leaves

Site	V	Mn	Co	Ni	Cu	Zn	Pb	Br
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	2.05	0.98	0.95	2.22	0.96	0.96	2.23	2.59
3	1.84	0.63	0.80	1.06	0.97	0.72	0.41	2.60
4	2.16	0.83	1.00	1.72	1.82	2.95	1.31	3.44
5	1.33	0.94	1.01	1.34	3.72	1.77	2.01	3.38
6	3.43	0.89	0.90	2.20	1.37	1.25	1.14	2.71
7	2.17	0.78	0.97	1.51	1.16	1.25	2.82	2.09
8	2.57	1.05	0.99	2.79	1.53	1.31	1.50	4.91
9	2.56	0.69	0.88	1.11	0.91	0.97	1.20	0.85
10	1.87	0.87	0.97	6.17	2.25	1.58	1.94	3.28
11	1.16	0.46	0.99	1.34	0.78	1.46	1.29	2.13
12	1.43	0.74	0.96	2.61	3.77	2.15	1.74	2.13
13	3.63	0.93	0.98	2.43	0.58	0.90	1.05	1.16
14	1.80	0.69	0.86	1.63	0.97	1.48	3.07	2.34
15	2.03	0.72	0.93	2.60	2.40	2.85	4.62	5.13
16	2.00	1.35	0.96	1.96	2.50	1.38	1.40	3.50
17	2.83	0.70	0.90	1.00	0.64	0.91	1.15	2.56
18	1.81	0.60	0.93	1.05	0.68	0.84	0.98	4.85
19	1.61	0.49	0.88	1.92	1.20	1.75	1.16	1.49
20	2.90	0.92	1.04	1.75	6.91	2.89	1.99	1.99
21	1.78	0.64	0.88	3.22	1.11	2.21	1.95	2.54
22	2.42	1.15	1.12	5.72	1.43	2.11	2.18	3.46
23	2.03	0.83	1.02	0.91	0.90	1.10	1.40	1.48
24	2.48	0.66	0.95	1.06	0.76	1.22	1.80	1.56
25	3.27	0.86	1.04	1.31	2.05	1.45	1.44	1.27
26	2.97	0.82	1.08	2.63	2.15	2.51	1.69	2.02
27	2.99	0.61	1.07	1.94	1.81	4.07	0.98	8.25
28	2.43	0.90	0.92	4.35	0.96	1.30	1.29	2.77
29	2.84	0.53	0.95	0.65	1.01	1.16	0.70	1.44
30	4.80	1.38	1.00	1.26	2.04	1.20	1.22	3.90
31	3.10	1.71	1.07	1.19	0.84	1.64	1.25	3.92
32	2.09	0.69	0.94	1.42	0.79	1.37	0.95	3.45
33	1.56	0.88	0.95	1.24	2.27	2.22	2.32	3.24
34	1.17	1.20	1.01	2.61	1.36	1.92	2.17	2.88
35	1.85	1.25	1.05	3.38	1.17	1.14	1.82	2.27
36	1.70	1.14	1.02	5.39	1.36	3.40	5.71	3.31
37	3.21	1.97	1.01	2.39	4.11	1.64	1.18	2.66
38	2.41	0.83	0.81	2.12	1.13	1.46	1.34	2.68

II). The differences observed between these species suggest that there is a differential accumulation of the metals between the species used as biomonitors. Regarding this, a selective uptake of cationic metals has been observed in lichen species used as biomonitors that depends on the type of union established between these metals and the ligands present on the surface of the biomonitor (Carreras et al., 2005). However, in order to confirm this hypothesis a series of laboratory tests must be undertaken with these species.

3.2. Contamination factor and correlations

In order to determine the association between the accumulation of elements and the environmental variables characteristic of each sampling point, correlation coefficients (Spearman and Pearson) were calculated for each species between the CF of each element, the categories of the environmental variables and the different elevations.

For *T. capillaris* (Tables 6 and 7), the CFs calculated for V, Co, Ni, Cu and Zn were positively correlated with the Urban-Industrial category. Among these metals, both V and Co appeared to be associated with soil particles as indicated by the cluster analysis (Fig. 2). However, when the values were normalized subtracting the "soil effect" in the calculation of the CFs, significant positive correlations were found between these elements and the anthropogenic activities. This indicates that even though the soil particles are providing part of these metals, their origin could also be anthropogenic. Vanadium is considered a toxic element (Moskalyk and Alfantazi, 2003) and high levels of atmospheric vanadium are associated with industrialized areas, especially in those where fossil fuel is burned (Seiler et al., 1994). This element has increased during recent years in urban environments due to industrial dusts (Manta et al., 2002). The main sources of atmospheric emission of Ni and Cu are from the use of fossil fuels and the industrial production of Cu–Ni (Nriagu and Pacyna, 1988). Carreras and Pignata (2002) have also reported high levels of Ni and Cu in transplanted *U. amblyoclada* lichens in an industrial area of Córdoba. On the other hand, Pb, Zn and Cu can be identified as tracers of anthropogenic pollution as Manta et al. (2002) showed in Italian soils.

The values of CFs for Zn correlated with the Urban Industrial and Road variables, showing the important contribution by urban emissions and traffic as previously reported by many authors (Christensen and Guinn, 1979; Rapsomanikis and Donard, 1985; Beckvith et al., 1985; Ward, 1989). These results are also in accordance with those of Pignata et al. (2002), who reported

Table 7
Rank correlation coefficients between the contamination factors (CFs) and the environmental variables in *T. capillaris*, excluding the control site ($n = 37$)

CF	Elevation	Agricultural	Urban-Industrial	Roads
V	−0.075	−0.091	0.406*	−0.023
Mn	−0.225	0.332*	0.277	0.112
Co	−0.047	−0.002	0.522**	0.290
Ni	0.124	−0.001	0.475**	0.200
Cu	0.158	−0.087	0.343*	0.289
Zn	−0.029	−0.153	0.440**	0.448**
Pb	0.015	0.171	0.246	0.388*
Br	−0.176	0.180	0.208	0.110

$^*P \leq 0.05$; $^{**}P \leq 0.01$.

Table 8
Contamination Factor (CFs) values of V, Mn, Co, Ni, Cu, Zn, Pb and Br measured in *T. permutata* leaves

Site	V	Mn	Co	Ni	Cu	Zn	Pb	Br
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
4	2.62	1.28	1.40	2.86	1.70	2.02	6.00	3.12
5	2.80	1.77	1.66	1.89	1.73	2.41	8.09	4.52
6	2.70	0.95	1.11	1.73	1.71	2.82	3.93	2.35
7	3.17	2.34	1.32	2.69	2.61	3.13	8.85	1.45
8	1.63	0.96	1.14	2.46	1.93	1.31	1.89	1.07
9	2.46	1.62	1.19	1.94	0.98	2.52	5.29	1.79
10	1.31	1.93	1.33	2.45	2.77	2.96	9.38	6.17
11	1.29	1.72	1.19	2.16	1.96	2.14	10.00	2.74
12	3.10	1.75	1.17	4.26	1.87	2.80	4.30	2.87
13	4.19	2.94	1.26	11.06	2.20	3.93	9.53	2.41
14	3.97	1.45	1.06	1.09	2.36	2.92	12.22	2.72
16	2.01	2.67	1.30	4.22	1.69	2.69	6.05	2.35
17	2.01	0.95	1.07	0.56	1.03	1.39	2.38	1.64
18	1.19	1.26	1.07	1.04	1.07	2.03	4.12	2.10
19	1.69	1.79	1.16	1.33	0.98	2.30	4.92	1.40
20	3.04	1.09	0.99	1.76	1.34	2.47	3.98	3.46
21	1.88	1.60	1.12	1.67	1.60	3.41	5.66	1.60
22	1.85	1.41	1.17	0.86	2.35	2.59	6.45	2.41
24	2.47	1.39	1.16	1.38	1.65	1.84	5.00	1.14
25	1.86	0.79	1.17	1.85	0.52	1.02	4.80	1.56
26	5.95	1.97	1.22	2.77	2.73	3.36	7.05	3.20
27	2.26	1.88	1.23	1.20	3.74	4.69	10.26	3.60
28	2.37	2.00	1.29	1.04	1.54	2.68	10.15	1.59
29	3.22	1.21	1.20	2.00	2.23	2.57	6.69	1.97
30	2.34	2.43	1.36	1.27	0.86	1.76	5.42	1.84
31	2.78	1.89	1.17	0.65	0.73	1.62	4.21	5.06
32	1.99	1.70	1.22	1.12	3.10	3.40	4.45	1.67
33	3.90	2.04	0.94	2.33	0.85	4.05	9.20	3.75
34	1.81	1.62	1.13	5.39	0.81	2.20	4.50	2.53
36	2.04	2.29	1.04	3.15	1.47	5.96	7.71	3.01
38	2.46	1.89	1.24	2.35	4.88	3.53	5.54	2.13

elevated levels of Zn in a biomonitoring study using *T. capillaris* undertaken in the city of Córdoba and its industrial surroundings.

Regarding the CFs for lead, a positive correlation was found with the variable Road suggesting that the origin of this metal is associated with vehicle emissions. It is important to note that the use of leaded gasoline in Argentina has now been reduced for over a decade. However, the results indicate the existence of elevated levels of Pb associated with soils near roads, probably as a result of the use of tetramethyl and tetraethyl Pb as an antiknock gasoline additive in the past (Garty, 2001).

The CFs for Mn were the only ones that had any correlation with the agriculture variable, suggesting that this metal could be related to the use of agrochemicals (fertilizers and pesticides) that has noticeably increased in Argentina over the last years. On the other hand, the atmospheric levels of this metal could also be reflecting an increased availability of Mn, normally a major component of the soil, as a result of the erosion caused by the intense agricultural use to which the earth is submitted. Phosphate fertilizers are manufactured from rock phosphates and, according to their origin, could contain various trace and minor elements (Giuffré de López Camelo et al., 1997). Similarly, Gimeno-García et al. (1996) found higher levels of Fe, Mn, Zn and Ni as impurities in fertilizers in Spain.

In studies undertaken in the south of Argentina the thalli of lichens were found to be enriched with Br, Cr, Sr, Hg, Pb, Sb, V and Zn (Calvelo et al., 2002). In the province of Córdoba, the main source of Pb and Zn is considered to be from industries (Carreras and Pignata, 2002), although Calvelo and Liberatore (2004) have found increased levels of Br, Cr, Pb, Sb, V and Zn in lichens in the south of Argentina and associate this enrichment with contamination generated by traffic.

No significant correlations were found between the CFs of the elements analyzed in *Tillandsia* and elevation, even though studies undertaken with lichen thalli by Bergamaschi et al. (2002) have shown that elements with high values of enrichment factor (EF) such as Br, Pb and Zn, seem to have some sort of relation with elevation, showing a slight increase in their concentrations at higher elevations. These authors suggest that it is possible that part of these elements are associated to the finer air-borne particles and can therefore be subjected to a distant transport phenomenon in the higher troposphere strata. However when analyzed, neither *T. permutata* nor *T. capillaris* showed any significant correlation between their CFs values and the different elevation levels of the study area.

The analysis of correlation undertaken in *T. permutata* (Tables 8 and 9) showed positive correlations between the values of the CFs of Zn with the Urban-Industrial variable and the CFs values of Pb with the road variable. These results are in accordance with the results of the cluster analysis that includes these metals

Table 9
Rank correlation coefficients between the contamination factors (CFs) and the environmental variables in *T. permutata*, excluding the control site ($n=31$)

CF	Elevation	Agricultural	Urban-Industrial	Roads
V	0.006	0.102	0.233	0.175
Mn	0.112	0.158	0.357	0.256
Co	0.072	−0.085	0.231	−0.056
Ni	0.176	0.073	0.256	0.220
Cu	−0.230	0.004	0.278	−0.091
Zn	−0.207	0.182	0.433*	0.284
Pb	0.069	0.038	0.357	0.416*
Br	−0.077	0.213	0.270	0.323

$^*P \leq 0.05$; $^{**}P \leq 0.01$.

in the group of elements with anthropogenic origin. However, this species has a lower capacity of accumulation than *T. capillaris* with respect to the different categories of emission sources.

4. Conclusions

Significant differences were found between the uptake rates of the species studied. The ability to incorporate elements with respect to their emission sources was greater in *T. capillaris*, suggesting that this species is a better biomonitor with a more faithful representation of the elements associated with emission sources. Concerning the association between the elements and the different anthropogenic activities, increased levels of Pb and Zn were found to be related to vehicular emissions. The urban industrial activity also contributed to the presence of V, Co, Ni, Cu and Zn according to the enrichment pattern observed in *T. capillaris*.

Acknowledgements

This work was partially supported by the Agencia Nacional de Promoción Científica y Tecnológica (FONCyT), Brazilian Synchrotron Light Source (LNLS) and by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

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